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Influence of electron beam irradiation on crosslink behaviour of reclaimed tire rubber/EVA blend in the presence of radiation sensitizers

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Abstract. Non-degradable waste tire generation around the world is growing at an alarming rate. Diversifying the recycling route of these waste tires is essential to solve the problem. To address the issue, this study utilized radiation sensitizers and electron beam irradiation to enhance the poor properties of reclaimed waste tire rubber/poly(ethylene vinyl acetate) (RTR/EVA) blend. The RTR, EVA and radiation sensitizers were mixed in the internal mixer followed by electron beam (EB) irradiation with doses ranging from 50 to 200 kGy. Radiation sensitizers loading was fixed at 4 wt%. The degradation and stability in RTR were studied in term of crosslink behaviour upon irradiation. Electron beam irradiation revealed the presence of radical stabilizing and scavenging additives within RTR which retards the crosslinking process in RTR and the blends. RTR, EVA and the RTR/EVA blend suffered from further oxidative degradation from irradiation in air. Radiation sensitizers, trimethylol propane triacrylate (TMPTA) and tripropylene glycol diacrylate (TPGDA), were used to accelerate the irradiation induced crosslinking in RTR and the RTR/EVA blend. Presence of radiation sensitizers leads to enhanced crosslink formation within RTR and the RTR/EVA blend. These findings validated the feasibility of using ionizing radiation in the presence of radiation sensitizers for recycling inferior waste polymers into higher quality material.

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1 Introduction

Ionizing radiation is an upcoming powerful technology in addressing polymeric waste issues. The extent of irradiation can be controlled to introduce chain crosslinking or scission to tweak a recycle material's properties as desired. Previous publications [1,2] have addressed the lack of efficiency in radiation induced crosslink formation in reclaimed tire rubber and ethylene vinyl acetate (RTR/EVA) blends due to readily present radical stabilizing and scavenging additives in RTR. This study is dedicated to the use of different radiation sensitizers to accelerate radiation induced crosslinks in RTR/EVA blends. The three radiation sensitizers used are N,N-1,3 Phenylene Bismaleimide (HVA2), trimethylol propane triacrylate (TMPTA) and tripropylene glycol diacrylate (TPGDA) with two, three and two functional sites, respectively. The chemical structure of all three radiation sensitizers are shown in Figure 1. The loading of the radiation sensitizers has been set to 4 phr based on previous studies [3-5]. Presence of radiation sensitizers would allow for faster reach to optimal irradiation dose and reduce the undesired effect of oxidative degradation. The influence of electron beam irradiation and radiation sensitizers on crosslink network and the gel content properties are reported in this study.

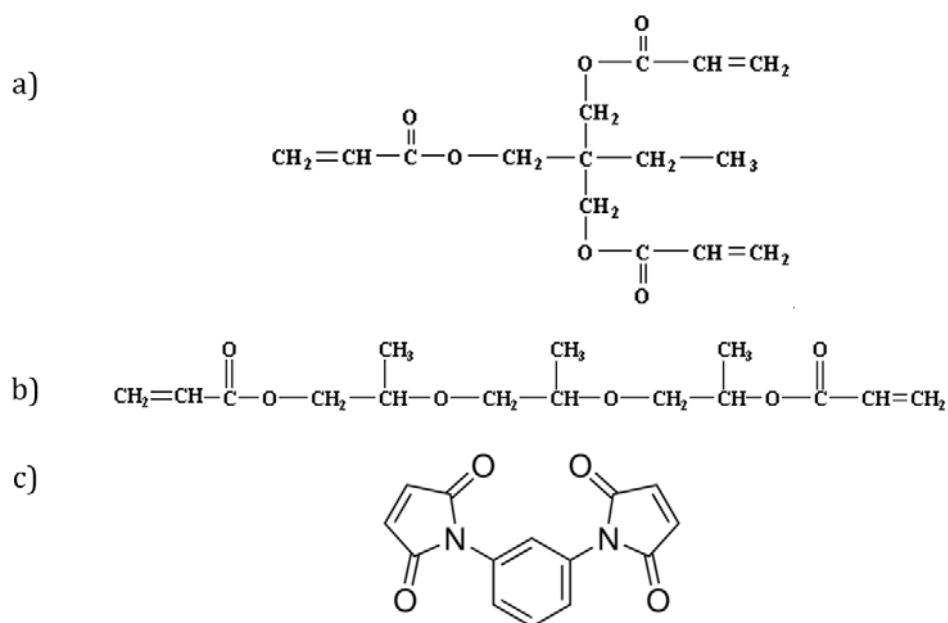


Fig. 1. Chemical structure of a) TMPTA, b) TPGDA and c) HVA2

2 Materials and Methods

2.1 Materials

Poly(ethylene-co-vinyl acetate) (Grade EVA N8045), EVA, having 18% vinyl acetate content with melt flow index, MFI, value of 2.3 g/10 min and a density of 0.947 g/cm³ was purchased from the TPI POLENA Public Limited Company, Thailand. Reclaimed tire

rubber (RECLAIM Rubberplas C), RTR, from waste, heavy duty tires used in this study was supplied by Rubplast Sdn. Bhd., Malaysia. General properties of the RTR are 48% rubber hydrocarbon, 5% ash content, 15% acetone extract, 25% carbon black fillers and density of 1.3 g/cm³. (3-Aminopropyl)triethoxy silane (APS) was used as compatibilizers in RTR/EVA blends. Multifunctional acrylates (MFA); trimethylol propane triacrylate (TMPTA) and tripropylene glycol diacrylate (TPGDA) were used as irradiation sensitized crosslinking agents. Whereas N,N'-1,3 Phenylene Bismaleimide (HVA2) was used as a conventional irradiation sensitized crosslinking agent.

2.2 Melt compounding

RTR and EVA were melt blended in an internal mixer (Brabender Plasticoder PL2000-6 equipped with co-rotating blades and a mixing head with a volumetric capacity of 69 cm³). The rotor speed was set at 50 rpm while blending temperature was set at 120 °C. The processing parameters were determined from a preliminary work.

Melt compounding was done according to the designation of the prepared blends as shown in Table 1. APS was added based on rubber weight percentage while radiation sensitizers were added based on total matrix weight percentage. EVA was fed into the internal mixer chamber and allowed to melt for two minutes, followed by the addition of RTR. Both EVA and RTR were allowed to mix for 8 minutes before collecting the blends from the internal mixer. Compatibilizer (when used) was added simultaneously with RTR at the second minute. Multifunctional acrylates and bismaleimide crosslinking agents (when used) were added at third and seventh minute respectively. Bismaleimide crosslinking agent was added later as it induces crosslinking process in polymers beyond 70 °C; unlike multifunctional acrylates which would only crosslink with exposure to irradiation energy. This ensures the compounded materials can still be processed (or flowing) during subsequent compression moulding step. Total mixing time was kept constant to 10 minutes for EVA, RTR and all the blends to ensure similar thermal history. The collected materials were immediately cut into smaller pieces and kept in sealed plastic bags for compression moulding process.

2.3 Compression moulding and electron beam irradiation

Materials obtained from internal mixer were compression moulded to obtain test specimens. The compounded materials were placed into a steel frame mould covered by aluminium plates at both sides. The materials were pressed at 130 °C into sheets of 1 mm thickness. The moulding cycles involve 3 minutes of preheating without pressure, 20 seconds of venting and 3 minutes of compression under 14.7 MPa pressure using hot and cold pressing machine (LP-S-50 Scientific Hot and Cold Press). Cooling was done immediately between two platen of cold press at 20 °C for 2 minutes.

The moulded sheets were irradiated using 3 MeV electron beam accelerator (model NHV-EPS-3000) at dose ranging between 0 – 200 kGy. The acceleration energy, beam current and dose rate were 2 MeV, 2 mA, and 50 kGy per pass, respectively

2.4 Gel content analysis

The samples gel content was determined according to ASTM D2765. Samples were placed in a stainless steel wire mesh of 120 mesh size and extracted in boiling Toluene using Soxhlet apparatus for 24 hours. Samples were then collected and dried in an oven at 70 °C

until constant weight is obtained. Gel content was calculated as per Equation 1 below. Where W_0 and W_1 are the dried weight of sample before extraction and after extraction, respectively

$$\text{Gel content (\%)} = (W_1 / W_0) \times (100) \quad (1)$$

Table 1. Designation of prepared samples

Designation	RTR (wt%)	EVA (wt%)	APS (wt%)	Radiation sensitizers (wt%)
RTR	100	0	0	0
RTR/TPMPA	100	0	0	4
RTR/TPGDA	100	0	0	4
RTR/HVA2	100	0	0	4
EVA	0	100	0	0
EVA/TMPTA	0	100	0	4
EVA/TPGDA	0	100	0	4
EVA/HVA2	0	100	0	4
50RTR	50	50	0	0
50RTR/5APS	50	50	5	0
50RTR/5APS /TPMPA	50	50	5	4
50RTR/5APS /TPGDA	50	50	5	4
50RTR/5APS /HVA2	50	50	5	4

3 Results and Discussion

Figure 2 shows the influence of TMPTA, TPGDA and HVA2 on radiation induced gel formation in RTR, EVA and 50RTR/5APS blend as a function of irradiation dose. Neat RTR shows 68% of the gel content prior to irradiation (0kGy), affirming the presence of

readily existing crosslinks within its matrix. The gel content of neat RTR increased only marginally with the increase in irradiation dose. Similar findings by Ratnam *et al.* [6] explained the stabilization of the rubber and the radical scavenging effects by the additives causing a marginal increment in the gel content upon irradiation. Presence of radiation sensitizers helped to enable more crosslink formation, yielding higher gel content values. RTR/HVA2 shows about 20% increase in gel content compared to neat RTR at equivalent irradiation dose, netting a maximum value of 91% gel content at 200 kGy irradiation dose. Addition of HVA2 proves to be efficiently introducing crosslinking in RTR sample. Similar observation has also been reported in EVA/NR study [7].

However, dynamically vulcanized RTR/HVA2 samples were found to undergo degradation during blending process. Thus, these made it difficult for RTR/HVA2 formulation to be compression moulded into testing specimens. Hence, influence of HVA2 on RTR properties could not be verified. TMPTA and TPGDA containing RTR sample also displayed higher gel content than neat RTR. This indicates that presence of TMPTA and TPGDA accelerates irradiation induced crosslinking in RTR [8]. RTR/TMPTA records higher gel content values as compared to RTR/TPGDA. This is due to the higher number of functionalities in TMPTA (trifunctional) contrast to TPGDA (difunctional) [9-10]. TMPTA is capable of forming more crosslink bridges due to higher functionality resulting in higher gel content values.

Figure 2b shows the influence of TMPTA, TPGDA and HVA2 on gel formation of EVA matrix. TMPTA was found to be the most efficient radiation sensitizer in accelerating formation of the crosslinks on EVA matrix compared to TPGDA, HVA2 and neat EVA. TPGDA and HVA2 only displayed slight increase in gel content values compared to neat EVA (inset of Figure 2b). These finding suggest the efficiency of crosslink formation in EVA matrix are in the order of TMPTA>TPGDA=HVA2. This is again due to difference in the functionality of radiation sensitizers as mentioned earlier. Unlike RTR/HVA2, no crosslink formation was observed in EVA/HVA2 composition before irradiation. HVA2 with multi-radical accepting capabilities interacts with radicals to stabilize the overall reaction. This suggests the presence or formations of radicals are more likely happening in RTR aided by the heat energy available during blending and compression moulding process. Whereas EVA is accounted as more stable at the processing temperature, leading to lower possibility for crosslink formation in EVA/HVA2 composition before irradiation. Similar observation has also been reported by [7]. Moreover, previous work has shown that HVA2 have higher tendency to interact with rubber component than the thermoplastic matrix used in the study [7,11].

Figure 2c shows the influence of TMPTA, TPGDA and HVA2 on gel formation of 50RTR/5APS blend. Gel content yield of neat 50RTR blend was also shown on the figure for comparison. It is observed that the 50RTR blends require an irradiation dose above 50kGy in order to achieve a significant increase in the gel content. This could be due to the presence of additives in the RTR retarding the crosslinking process in these blends as discussed earlier. At above 100kGy irradiation dose, the gel content of the 50RTR blend increases slowly and exhibits a marginal difference. 50RTR/5APS blend, the APS compatibilized blend, showed an interesting result where the gel content before irradiation (0 kGy) recorded lower values compared to the control, 50RTR blend. Gel content observed before irradiation in a blend was a contribution from the partially devulcanized structure of RTR. An obvious reduction in the gel values of APS compatibilized blends suggests that APS plays major role in further devulcanizing or reclaiming the RTR. This is supported by the fact that amines have been long used as reclaiming agent in rubber materials due to its strong nucleophilic nature [12-14].

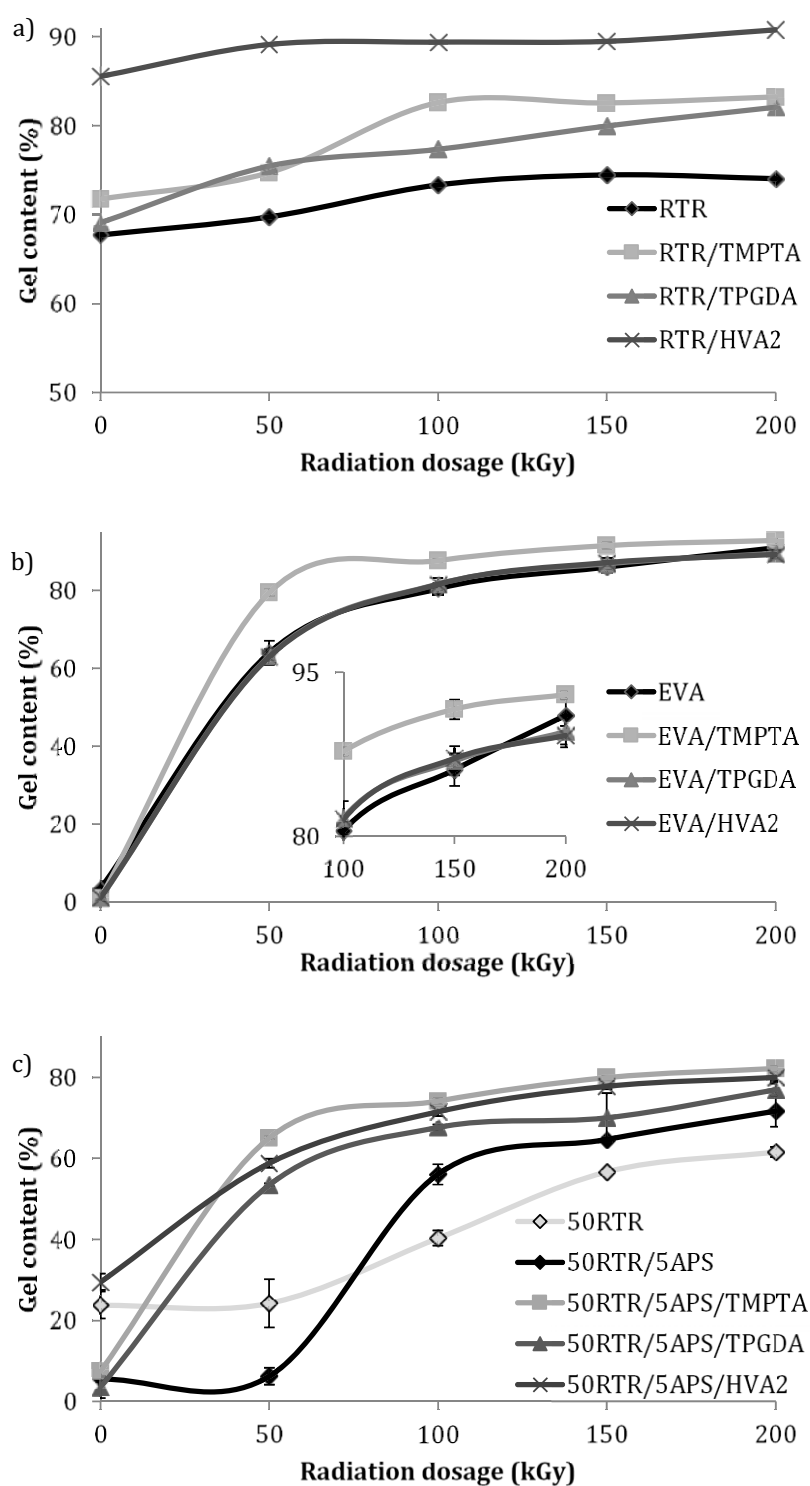


Fig. 2. Gel content values of a) RTR, b) EVA and c) 50RTR/5APS blends as a function of radiation sensitizers and radiation dose

Presence of radiation sensitizers has completely resolved the delay in crosslink formation observed in neat 50RTR and 50RTR/5APS blends. Upon irradiation of the 50RTR/5APS blends, TMPTA was found to yield the highest gel content values, closely followed by HVA2 and TPGDA. Before irradiation (0 kGy), a gel content value of 29.5% was observed in 50RTR/5APS/HVA2 composition. Judging from the gel content analysis of RTR and EVA in the presence of HVA2, the gel value observed in 50RTR/5APS/HVA2 composition could be mostly due to crosslink formation in RTR component of the blend. These observations suggest that the use of radiation sensitizers enhance the crosslink formation in the 50RTR/APS blends.

Charlesby-Pinner equation was used to determine the ratio of chain scission to crosslinking (p_0/q_0) in RTR, EVA and 50RTR/5APS blends in the presence of radiation sensitizers. The p_0/q_0 values have been listed in Table 2. In general, RTR showed the highest p_0/q_0 ratio, while EVA showed the lowest value and the blends showing an intermediate value. The p_0/q_0 values above 1 indicates the dominance of chain scissioning over crosslinking within the matrix. Presence of TMPTA and TPGDA in RTR decreased, while HVA2 further increased the p_0/q_0 values compared to neat RTR. The p_0/q_0 value of RTR/HVA2 was 1.93 indicating about 2 scissions could be happening per crosslinking in the RTR matrix, which would lead to substantial decrease in the molecular weight of RTR matrix. This further corroborates the reasons for difficulties in moulding RTR/HVA2 samples. Although RTR/TMPTA and RTR/TPGDA recorded a decline, the p_0/q_0 values were still higher than 1, indicating chain scissioning still dominates over crosslinking in the RTR matrix even in the presence of radiation sensitizers.

Table 2. Values p_0/q_0 of RTR, EVA and 50RTR/5APS blends in the presence of radiation sensitizers.

Designation	Neat	TMPTA	TPGDA	HVA2
RTR	1.8724	1.7718	1.7920	1.9255
EVA	0.2473	0.2723	0.2740	0.2805
50RTR/5APS	0.5478	0.6700	0.6960	1.0908

Both EVA and 50RTR/5APS blends displayed a slight increase in p_0/q_0 values in the presence of all three radiation sensitizers. This is to be expected as crosslinking process was found to have already effectively take place in the neat EVA and 50RTR/5APS matrix upon irradiation. Whereas the addition of radiation sensitizers would enhance the crosslinking process to a certain absorbed radiation dosage, upon which, chain scission are deemed to prevail. Presence of radiation sensitizers would allow for optimal crosslinking to be achieved at a lower absorbed dose of irradiation [15-17]. Among all the three radiation sensitizers, HVA2 recorded p_0/q_0 values above 1 for RTR and 50RTR/5APS blends. This indicates the 4phr of HVA2 loading used in this study is more than enough for RTR based system, leading to domination of chain scission. Optimization of HVA2 loading and blending parameters is essential to observe neat crosslink formation in irradiated 50RTR/5APS/HVA2 blends.

4 Conclusion

Formation of crosslink network and enhancement of gel content can be achieved in irradiated RTR and RTR/EVA blend in the presence of radiation sensitizer. TMPTA and TPGDA did perform excellently to increase crosslink network and gel content of RTR/EVA blend. HVA2's role in enhancing crosslink network in RTR/EVA blend could not be confirmed due to excessive loading of HVA2 in the blends.

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